An Investigation into the Feasibility of Capturing Carbon Dioxide
Directly from the Atmosphere

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Introduction

Carbon dioxide emissions to the atmosphere have risen steadily since the beginning of the industrial revolution. Furthermore, conservative estimates suggest that the world energy demand will double by the middle of this century[1]. Energy demand in the developing countries is growing by 3.5% per year, much faster than in the developed world, with these developing countries currently emitting 30% of the global total. World wide, carbon dioxide emissions are expected to exceed 36 billion tons of carbon dioxide per year by the year 2020[2]. Even though these forecasts may not be very accurate, the fact remains that tens of billions of tons will be emitted on an annual basis. It is reasonable to expect that, if there is a reduction, it will occur gradually and may not start in earnest before 2020. Carbon dioxide emissions will continue for the foreseeable future.

Carbon sequestration technology aims at preventing the accumulation of carbon dioxide by capturing it and putting it in safe and permanent storage. The obvious targets for carbon dioxide capture are large point sources, which offer high concentrations of carbon dioxide in controlled systems. These sources provide the most cost effective options for collecting carbon dioxide, but they do not account for all emissions. There are many distributed sources such as in the transportation sector. Eventually these sources will have to be addressed as well. Rather than eliminating them, one might consider the capture of carbon dioxide from the air after the emission.

Air extraction can be defined as the removal of carbon dioxide from the atmosphere. Air extraction can be viewed as a variation of flue gas scrubbing with the constraint that the source gas is at atmospheric temperature, pressure, and at ambient concentration of carbon dioxide. Air extraction technology would make the existing transportation infrastructure sustainable. It would also mitigate emissions from other smaller sources unsuitable for direct capture. As such the extraction effort would have to be able accommodate approximately 30 percent of current US emissions or ~1.5 Gt of carbon dioxide[3].

The Rationale for Air Extraction

Air extraction decouples sequestration from carbon dioxide emission, spatially as well as temporally. This is made possible by the rapid mixing of the atmosphere and the relatively high initial concentration of carbon dioxide in the atmosphere. Even at a high population density of 250 people/km^2 and US energy consumption, it would take in excess of one year to produce emissions that equal the atmospheric load over the area. Air, however, travels continental distances in a matter of days and mixes along a line of constant latitude within weeks. As a result, even in areas of high emissions carbon dioxide levels tend not to be much higher than the

world average. Globally, the atmosphere mixes in a couple of years[4]. Given that the current atmospheric rise in carbon dioxide concentration is around 2 ppm per year, there is no penalty associated with carbon dioxide capture far away from the source. Air extraction could occur at any place in the world.

Air extraction cannot replace capture of carbon dioxide at a concentrated source like a power plant. Clearly it is advantageous to capture carbon dioxide before it is let out into the air, since the cost of retrieving carbon dioxide from a dilute stream is always higher than retrieval from a concentrated stream.   On the other hand, air extraction can augment carbon dioxide capture at a power plant.   For example, President Bush has set a goal of creating a plant that can capture its own carbon dioxide within the next five years. This plant would use coal to produce hydrogen and subsequently produce power. The plant will sequester at least 90% of the carbon dioxide it produces[5]. The remaining CO_2 will still be released to the atmosphere. 10% of the emissions from a 1 GigaWatt coal plant operating at 40% efficiency would still amount to 750,000 tonnes of CO_2 per year. Additionally, this new plant would have to be situated near a geological formation suitable for sequestration. If existing plants were to be retrofitted then the carbon dioxide would have to be transported to the disposal site. Even if the plant is constructed adjacent to a disposal site, the lifespan of the plant may exceed that of the disposal site. Given the cost of pipeline construction, certain disposal sites may not be feasible if the distance is too large or the capacity too small. Given the highly heterogeneous nature of geological formations, a site that seemed suitable for sequestration may develop complications forcing on-site power plants to send their carbon dioxide elsewhere. Ocean disposal also involves pipelines to the abyssal plains or trenches. The demand for long distant transport of carbon dioxide or the transport of carbon dioxide through highly urban areas pose serious challenges and the required expensive infrastructure may prove to be a hindrance. If the cost of carbon dioxide extraction from air can be driven sufficiently low, air extraction could be of use in these situations.

As previously stated, much of the global carbon dioxide emissions emanate from large, concentrated sources. The smaller sources are, by and large, in the transportation sector, where collection at the source is usually impractical. On-board sequestration in the transportation sector would pose significant engineering problems. Fundamental changes in the design of an automobile would be required to capture the carbon dioxide and store it on board. Furthermore, the storage demand on board of a vehicle would be daunting.   For every 14 mass units of gasoline, the combustion process generates 44 mass units of carbon dioxide, which as a gas is also far more difficult to store than liquid gasoline, making the empty storage container far more massive than an ordinary gasoline tank. In addition, a new infrastructure, similar to gas stations, would be required to collect the spent sorbent and transfer it to a central sequestration facility.

Avoiding the complications of a carbon dioxide recovery infrastructure is the great advantage of using hydrogen as a transportation fuel. However, a hydrogen based transportation infrastructure would also have to be built from scratch. Hydrogen does not exist in nature and would have to be produced in a plant and then distributed to refueling stations. This process involves an energy penalty in converting the primary energy to hydrogen.   Additional costs are incurred relative to a gasoline based fuel system in that sufficient storage of hydrogen on board of a vehicle has proven to be difficult. The relevant question is whether or not the penalties, both in cost and energy consumption, are less than using conventional fuels and capturing the CO_2 from the atmosphere.

In comparing with a hydrogen transportation sector, it also makes sense to separate carbon dioxide capture from carbon dioxide disposal, as the latter would likely be shared by both approaches.   A hydrogen based transportation sector would likely use natural gas or coal to generate hydrogen and dispose of the carbon dioxide generated in the process at the site of hydrogen production.   A hydrocarbon based transportation sector would site the carbon dioxide

capture units at the same disposal site. Both processes would share the disposal technology. Thus disposal will not be included in the following discussion.

The transition to a hydrogen based transportation system would be a lengthy and costly effort.   Forcing the developing nations into a similar transition would severely hamper their economic development.   They may, however, have no choice if the developed nations abandon the current hydrocarbon based transportation systems.   If air extraction technologies could eliminate the environmental restrictions on a carbon based transportation system, the developing countries could use the most efficient means available to fuel their growth. The carbon dioxide issue could still be dealt with in developed countries.

Even if the future holds reduced carbon dioxide emissions, it may take a long time before the rise in carbon dioxide concentration is stopped. The IPCC has stated that potential climate change effects are likely to intensify and atmospheric levels of carbon dioxide may continue to rise for the foreseeable future.   Since the consequences of reaching any level of carbon dioxide are not yet fully understood, it would be extremely valuable to have in hand a technology that, at least in principle, would allow an independent reduction of atmospheric carbon dioxide levels.

We can summarize the reason for pursuing air extraction as follows:

1. It may prove to be an effective alternative to scrubbing and transporting CO_2 particularly for existing facilities that are ill suited for retrofitting or for locations that make transporting carbon dioxide from the source to the disposal site unfeasible.

2. In the early stages it may be coupled to the use of carbon dioxide in enhanced oil recovery.   Indeed the ability of setting air capture up at the oil field would open many remote oil fields for tertiary recovery. Remote coal bed methane sites may also benefit.

3. It would allow the existing infrastructure to live out its useful life.

4. The hydrogen economy may not be the most energy efficient option for eliminating dispersed carbon dioxide sources.

5. The temporal and spatial decoupling between carbon dioxide sequestration and emission, would allow the developing nations to make the transition at their own pace.

6. Developing nations could use existing technology to accelerate their development without fear of irrevocably closing options for carbon management.

7. Climate change concern may warrant carbon dioxide reductions rather than just carbon dioxide emission reductions.

The Specifics of Air Extraction

Air extraction refers to the removal of carbon dioxide from the atmosphere. The process starts with air containing 370 ppm carbon dioxide and finishes with pressurized CO_2.   The process does not include carbon dioxide disposal or storage. Of course, carbon dioxide capture from air is usually followed by carbon dioxide disposal or storage, but the choice of these options depends on local constraints and is not driven by the capture technology.
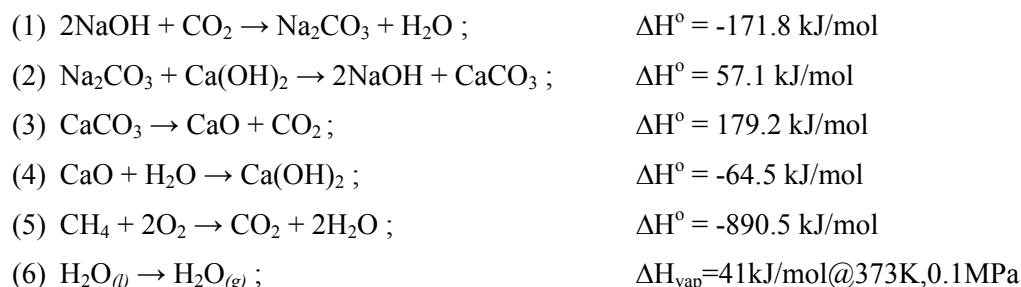
The most important observation to make regarding carbon dioxide capture from air is that the objective is not CO_2 free air, but CO_2 from the air. The CO_2 gradient is what drives the absorption and therefore complete extraction would be self-defeating. As carbon dioxide levels drop, the reaction kinetics is likely to slow down and complicate further reductions in CO_2 concentration. An analog is the leaf of a tree, which maintains a slightly reduced partial pressure of carbon dioxide on its surface and thus is capable of removing carbon dioxide from the air. Once carbon dioxide has been absorbed, a second processing unit will have to regenerate the sorbent and deliver the carbon dioxide in a pure and concentrated form. This stream is then readied for sequestration. This paper will not deal with the aerodynamic design of the capturing system. For purposes of this discussion it suffices to consider a cooling tower type design, where heat exchange has been replaced with carbon dioxide transfer, which follows a similar transport equation with similar transport coefficients.

In order to be somewhat more specific, we consider filter systems to be wetted by a flow of sodium hydroxide that readily absorbs carbon dioxide from the air and in the process turns into sodium carbonate. We note that if the pressure drop across the system due to viscous drag is comparable to the kinetic energy density in the air, then the fraction of carbon dioxide removed from the stream becomes significant, as long as the sorbent materials are strong absorbers. The reason for this simple relationship is that the momentum transfer to the wall follows essentially the same equation as the carbon dioxide transfer. A possible implementation is at a cooling tower of a nuclear power plant where the intake air is pulled through a filter system that is continuously wetted with sodium hydroxide. There are other options, where the slight pressure drop in the system is generated by other means. For example, a system where air gets in contact with sorbent surfaces simply by the wind passing through the device should also be considered.

The absorber component of the system has not been completely delineated. Ongoing studies will result in a detailed analysis of this aspect of the problem. Significant analysis is required to determine the optimum design for the contact system. The only hard design criterion is the rate of absorption. It should be noted that the volume of sorbent per unit output of carbon dioxide is independent of the details of the air contacting design. A number of lines of reasoning have repeatedly suggested that the cost of the capturing structure is small compared to the cost of sorbent recycling. Therefore the focus of this paper is on the second step. The only assumptions that enter into the analysis are the size of the capturing apparatus and the efficiency of the capturing process. The cost of this component is expected to lie with the structure and circulation system. The cost of the structure will be incurred in the financing costs. There will be an amount of sorbent lost per tonne of CO_2 extracted. In the case of sodium hydroxide, which is not volatile, one can assume that these losses are very small. Furthermore, sodium hydroxide can be readily produced from Trona, which is available naturally in large quantities. Therefore, makeup sorbent would be quite low in cost.

The focus of this investigation is on the second step of the process, the recovery of the sorbent. The conventional route of recovering sodium hydroxide from sodium carbonate, which is used in the paper industry and elsewhere, transfers the carbonate ion to calcium carbonate. The exchange between lime and sodium carbonate resulting in limestone and sodium hydroxide – at least in diluted streams is a well known process.

The capture process is described by the formation of sodium carbonate from sodium hydroxide and carbon dioxide from the air. This is followed by the recovery of the sodium hydroxide using calcium hydroxide. In this step, calcium hydroxide is converted into calcium carbonate. The calcium hydroxide is recovered by calcining the limestone precipitate and then slaking it with water. The individual reactions, along with free energy or enthalpy values, are listed below. The thermodynamic data was obtained from available literature[8].

(1) $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$; ΔH^o = -171.8 kJ/mol

(2) $Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$; ΔH^o = 57.1 kJ/mol

(3) $CaCO_3 \rightarrow CaO + CO_2$; ΔH^o = 179.2 kJ/mol

(4) $CaO + H_2O \rightarrow Ca(OH)_2$; ΔH^o = -64.5 kJ/mol

(5) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$; ΔH^o = -890.5 kJ/mol

(6) $H_2O_{(l)} \rightarrow H_2O_{(g)}$; ΔH_{vap}=41kJ/mol@373K,0.1MPa

In summary the system suggested here, uses caustic soda, sodium hydroxide as a sorbent. An aqueous solution can drip over internal surfaces in the filter system and thus allow for the capture of carbon dioxide from the air that passes through the system.   Once the sorbent solution has reached the bottom of the system, it is either re-circulated or removed from the system for recycling. The purpose of the recycling plant is to strip the carbon dioxide from the spent sorbent and return fresh sorbent to the capture device. After the carbon dioxide has been stripped, it is compressed and sent to a disposal site.

Overall Energy Balance

In considering this system in terms of its energy balance, one should compare it to the basic reaction of forming carbon dioxide.

$$C + O_2 \rightarrow CO_2 \; ; \Delta G^o= \text{-394.4 kJ/mol or 9GJ/tonne}[8]$$
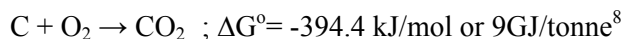
The heat of this reaction is given per tonne (metric ton) of carbon dioxide. The combustion processes that leads to the production of carbon dioxide typically generates more heat. Since nearly all of them involve not only the oxidation of carbon but to a smaller or larger extent the oxidation of hydrogen.   Heat of combustion values for carbonaceous fuels range from about 500 kJ per mole of C for coal to 890 kJ per mole of carbon for natural gas. This translates to 11.4 GJ/ tonne of CO_2 for coal and 20.2 GJ/ tonne of CO_2 for methane

If the energy penalty of the capture process is large, then it is important that the carbon dioxide generated in the capture process is not itself emitted to the air. This cannot be completely avoided; for example energy penalties associated with shipping raw materials to the disposal site are likely due to fuel consumption which itself requires air extraction. While these energy expenditures are likely to be small, it is important to realize that the carbon dioxide created in the sorbent recovery does not have to be let out into the atmosphere. Therefore it will not have to be subtracted from the net carbon dioxide captured, even though it will of course add to the total carbon dioxide that will need to be disposed of. The reasoning is not that different from the case of an hydrogen car, where upstream energy costs for example those encountered in the compression of hydrogen will not add to carbon dioxide emissions as long as they are captured, but the carbon dioxide captured in the process will have to be disposed of and thus raises the cost penalty involved in carbon sequestration.

The regeneration of sodium hydroxide from sodium carbonate will also require an input of energy. At present, the exact details for an engineering design are not known; however, transferring carbonate ions from sodium carbonates to calcium carbonates is an existing chemical process. It is currently being performed at the FMC Chemical Plant in Green River, Wyoming. The plant produces caustic soda directly from Wyoming Trona. The Trona is reacted with lime to form a dilute caustic solution and calcium carbonate[9]. The regeneration means suggested by the company is a lime kiln. A review of this process suggests that the bulk of the cost and energy demand will occur in the recycling of the calcium carbonate. The cost of mixing the solutions and filtering out the precipitate is assumed to be low. The primary chemical reaction in this process is the thermal decomposition of calcium carbonate, reaction (3).

The enthalpy of reaction (3) is 179.2 kJ/mol or 4.1 GJ/ tonne of carbon dioxide. This is the theoretical minimum energy penalty required to recycle the sorbent. It would be equally possible to express numbers in terms of tonnes of limestone or tonnes of lime. For every tonne of carbon dioxide that is freed from the sorbent, 2.3 tonnes of limestone enter the calcination process and 1.3 tonnes of lime leave the kiln. The value of 4.1 GJ/tonne of carbon dioxide is approximately 45% of the free energy released during the combustion of pure carbon. For natural gas this number would drop to 21%.

The calcination reaction is at the heart of the cement manufacturing industry. However, the typical cement making process is more energy intensive than simple line calcination, as it produces clinker at temperatures of up to 1800 K[10]. Indeed, in some designs cement kilns perform calcination in a preparatory step in order to reduce energy consumption. However, the overall efficiency regarding actual primary energy consumption to the theoretical limit can be scaled to the pure calcination process. The theoretical minimum energy consumption for clinker is 1.76 GJ/ tonne of clinker while the most efficient process, short dry kiln, requires 3.2 GJ/ tonne of cement[11]. The ratio of these values suggests an efficiency factor of 1.8 with respect to the theoretical limit. A major source of energy loses is radiative losses at these extremely high temperatures. Given that radiation is proportional to the temperature raised to the fourth power, the 400K difference between the two processes will lead to very different loses. If we compute the ratio of the radiation loses at the two end temperatures we obtain 0.2. This ratio can then be applied to the excess inefficiency (0.8) to obtain a scaled efficiency factor for simple calcinations of 1.16. By multiplying the theoretical energy consumption by the efficiency factor we obtain a reasonable calcinations estimate of 4.8 GJ/ tonne of CO_2. This value can now be used for cost estimating purposes. Calcination of limestone using a fluidized bed has been done on a pilot scale[12]. However, we do not have data for those trials.

The purpose of the paper is not to advocate sodium hydroxide with lime washing as the best possible solution to air capture, but by settling on one specific sorbent, it becomes possible to work out the difficulties and obstacles that arise from this choice. Furthermore, it provides a base system in which to identify and estimate cost.

A Preliminary Cost Analysis

The viability of the sorbent recovery process will be judged on the net carbon production and the cost, per tonne, of carbon dioxide. To this end, a preliminary evaluation will be performed in which various assumptions for losses and parasitic energy requirements are made. For example, it would be advantageous to have the pumping requirements met through renewable sources.

A conventional calciner system is not appropriate for calcining calcium carbonate in an air capture system, as it would emit a large amount of carbon dioxide to the atmosphere. There are several different approaches one could take to obtain heat without carbon dioxide emissions. Here we introduce a membrane process that uses a mixed conductor membrane (MCM) to keep the unused air separate from the combustion products[13]. The advantage to this system is that the combustion occurs in an O_2/CO_2 environment, thereby producing a pure stream of CO_2 rather than a mixture with N_2 and impurities. However, this system is in the early phases of development and cost estimates are not possible.

The principle, transporting oxygen across a membrane, is analogous to the solid oxide fuel cell (SOFC). A solid oxide based membrane system should be substantially cheaper than a solid oxide fuel cell, which uses similar types of membranes as electrolytes. Fuel cells in contrast to membrane separators must provide charge electrodes on the surfaces of these devices in order to carry the return current. In the membrane separators, the electronic back current is in effect short circuiting the cell. The Department of Energy's cost goal for the installation cost of solid oxide fuel cells aims at $1500 per kW, while the MCM investment target is ~ €400/kW or $450/kW.

The economic data for fuel cells will be used in the cost estimate. If treated as simple heat generators, these fuel cells could reach efficiencies of 80-85%[14]. As described above, waste heat will be very valuable in this process. A commercially available product is the PC25™ system manufactured by International Fuel Cells, LLC. This is a 200 kW fuel cell system that consumes 2100 cft/hr or 86 lbs/hr (39 kg/hr) of natural gas. The rated efficiency is 87% with 37% being electrical and 50% being thermal. The estimated installed cost is approximately $4500/kW with a start up cost of $15,000. Federal and state funding may be available and could amount to $1000/kW[15]. These specifications will be used for the calculations as the first generation SOFC's are currently unavailable and the DOE's performance target is for 2nd generation SOFC's. The most important difference with the commercial PC25™ is that the MCM or SOFC would operate at temperatures in the 1200-1300K range. These temperatures are suitable for calcinations and better suited for heat exchange. Operating costs will also depend greatly on the price of natural gas.   Current NYMEX prices are approximately $5.50/ million BTU[16], but more typical long time averages have been around $3.00 per million BTU.

The specifications listed above can be scaled down to a separation plant that has a thermal throughput of 100 kW equal to a power plant of 80% percent efficiency that would provide electricity and waste heat. The plant would have the characteristics listed in the Table 2. The primary energy is based on the free energy of methane combustion shown in reaction (5).

Table 2
Specifications for Feasibility SOFC Power Station

Specification	PC25™	Feasibility SOFC
Rating	200 kW	100 kW
Methane Throughput	39 kg/hr	16 kg/hr[17]
Primary Energy	17, 140 GJ/yr	7,020 GJ/yr
Installed Cost	$4,500 /kW$_e$	$4,500 /kW$_e$
Total Cost	$900,000	$450,000

Estimating the cost of a complete sequestration system is subject to much uncertainty given the amount of unknowns. One of the larger unknowns is the size of the capture devices and their design. This will not impact the cost of recycling the sorbent because the volume of sorbent is independent of the partial pressure. Given this uncertainty, it was deemed most appropriate to cost the system beginning at the downstream end, or the calciner. This is a reasonable procedure as the calciner station is the most expensive item. To maximize efficiency, it would be highly desirable to keep it operating continuously. We would then have to assume overall values for efficiency and availability as well as parasitic energy requirements. Parasitic energy refers to the energy required to operate all of the equipment aside from the calciner. For these calculations the overall efficiency was 80%, the availability was 99%, and the parasitic requirement was 1%. Given those values, the total available energy for calcining is approximately 5,500 GJ/year. If we assume the aforementioned 4.8 GJ/tonne for the calcining, we arrive at an annual CO_2 extraction of 1,150 tonnes. To check the assumption regarding the parasitic requirement, a simple calculation was performed to estimate the energy involved in lifting the sorbent material through an air contacter system. If we assume that the calcining occurs once per day and the sorbent solution concentration is 0.5 mol/l then we are required to circulate 140 m^3 of solution. An additional assumption of a 30m pumping height produces a daily consumption of 0.04 GJ. Given a factor 2 for inefficiencies we obtain an annual consumption of 30 GJ or 0.5%.

The calculated cost per tonne must include the loan repayment, the fuel costs, and maintenance costs. At a rate of 16 kg/hr, the calciner will consume 140 tonne/year at cost of $5.50/MMBtu. This translates into a total fuel cost of approximately $40,600 per year. If we assume the loan is repaid over 20 years at an annual interest rate of 5%, we obtain annual payments of $35,600 per year. This is based on the fuel cell cost of $4,500/kW. Assuming a 10% maintenance cost based on the loan, we obtain a preliminary estimate of $68/tonne. This does not include the cost of compression or sorbent replacement. If we include an energy penalty of 340 MJ/tonne for compression[18], the total additional energy requirement is 520 GJ. This is an 9% reduction in the energy available for calcination but includes the additional 386 tonne of CO_2 produced by combusting the methane. There will be a fraction of sorbent lost to the environment. The cost of Green River Trona is $105/ short ton f.o.b.[19]. If we assume an extremely conservative 1% loss of sodium hydroxide on 1150 tonne carbon dioxide, we would add $2 to the cost of the carbon dioxide extracted.

As expected, variations in the fuel and fuel cell costs will have dramatic effects on the cost per tonne. Table 3 contains a simple sensitivity analysis where the fuel and fuel cells costs are varied. The values in the table are cost per tonne extracted.

Table 3
Sensitivity Analysis

Variables		Cost per kW Installed		
Fuel Cost	Overall Efficiency	$4500	$1500	$500
$5.50 /MMBtu	80%	68	46	39
	90%	61	41	35
$3.00 /MMBtu	80%	52	30	23
	90%	46	27	20

These values do not include the cost of sorbent replacement, roughly $2 per tonne of CO_2 extracted. This could be compared with the estimate costs using monoethanolamine (MEA) of approximately €37-50/tonne[18], roughly $40-55 USD/tonne.

For sizing purposes, a daily material balance, in tonnes per day, has been prepared. The balance assumes that the incoming limestone contains 20%, by volume, water. The fuel cell is assumed to absorb 50% of the oxygen from the airflow. There are no figures for the sodium hydroxide as it is recycled within the system. In order to maximize the energy efficiency of the process it will be necessary to minimize heat loss. This will require an energy inventory in order to determine the optimal use of the heat produced by the process. As shown in Table 1 the lime leaving the reactor carries almost 1GJ of energy per tonne. The lime will be reacted with water to form slaked lime, an exothermic process which occurs at 500°C according to reaction (4).

For the initial calculations it will be assumed that the input temperature is 300K and the fuel cell temperature is 1200K. The theoretical calcinations temperature for calcium carbonate is approximately 1173K. The values for sensible heat reflect the energy consumed or released by changing the temperature of the various material streams. These numbers were calculated by integrating formulae for the specific heat, C_p, of each component. The specific heat data was obtained from the literature[8, 20]. Four reactions occur in the process; the evaporation of water from limestone, the calcination of limestone, the combustion of methane, the hydroxylation of calcium oxide. A daily material and energy balance is presented in Table 4. Energy consumed is positive and energy released is represented as a negative number, in parenthesis.

Table 4
Daily Material and Energy Balance

	Mass	Temperature		Energy	Sensible	Reaction
	(tonne)	Start	Finish	(kJ/mol)	(GJ)	(GJ)
Input						
$CaCO_3$ (s)	7.13	300	1200	169.79	12.10	12.77
H_2O (l)	1.28	300	374	5.60	0.40	2.90
N_2 (g)	9.67	300	1200	3.72	1.28	
O_2 (g)	3.10	300	1200	38.30	3.30	
CH_4 (g)	0.38	300	1200	56.18	1.35	(21.37)
Output						
CaO (s)	3.99	1200	800	(21.27)	(1.52)	
CO_2 (g)	4.19	1200	374	(41.41)	(3.95)	
N_2 (g)	9.67	1200	374	(3.57)	(1.23)	
O_2 (g)	1.55	1200	374	(35.97)	(1.55)	
H_2O (g)	0.86	1200	374	(32.08)	(1.54)	(1.95)
Calcium Hydroxide						
H_2O (g)	1.28	374	800	15.53	1.11	
$Ca(OH)_2$	5.27	800	374	(45.28)	(3.23)	(0.53)
Total					6.53	(8.18)
Grand Total						**(1.65)**

The first observation to be made is that the entire process is a net heat producer. However, there are no explicit losses built into the calculations. If we sum the absolute value of all the energy changes we obtain ~72 GJ, meaning the system can tolerate loses of up to 2%. The input water is the water contained in the limestone plus the amount required for the hydroxylation of the lime.

What Does it All Mean?

The process balance and preliminary cost analysis were done to show that the concept of air extraction is feasible. The most significant omission from the analysis is verification that the contact scheme, air to sorbent, will actually provide sufficient sodium carbonate to the reactors. The use of sodium hydroxide was chosen because it is an existing process that can be used in a feasibility study. Given the low cost power available in Wyoming, it may be assumed that optimization of the whole process is likely. The use of the novel technologies suggested in this paper will further increase the efficiency. This is not to say that sodium hydroxide is the ideal sorbent, only that we are assured it works. Indeed, finding a sorbent with a lower binding energy than limestone and that could be recycled in a single step would greatly improve the economics of the process. On the other hand, the economics of this capture process will only complete, once we account for all the costs. This paper only looks at the sorbent recovery cycle, which is thought to be the most expensive part of the system. Like most capture schemes there is a penalty associated with compression to a usable pressure. What this scheme avoids is the transportation costs. This is a significant sum, given that pipelines cost between $0.2 and $0.8 million USD per kilometer to build[18]. The transportation infrastructure will also require energy for maintenance.

This last point raises an interesting dilemma. In order to compare various methods of capturing carbon dioxide and sequestration, a system of carbon accounting will be needed. This system would have to start at the generation point and end with the monitoring costs associated with the sequestration site. Each direct capture method will reduce the efficiency of the plant in terms of parasitic energy. There will be costs associated with equipment, sorbent, and transportation. Sequestration will have costs associated with disposal and monitoring. The leakage rate and duration of the disposal will also require inclusion. These factors may not be reflected in the cost of sequestration. If we set a target of maximum efficiency in resource utilization then we must include everything, from start to finish. This also applies to a hydrogen economy as long as the energy source is carbonaceous fuels, such as the FutureGen plant. Such a system would allow for accurate comparison of the means through which we obtain our energy and mitigate the environmental consequences. There will be intangibles associated with these figures. The carbon dioxide will have to go somewhere causing land use changes and changes in the local environment.

The cost range of $21-$70 per tonne of carbon dioxide is compatible with the estimates made in Holland[18]. The wider range reflects the uncertainty in the technology and the processes involved. Also, this estimate is highly sensitive to the cost of natural gas. For example, if the wholesale cost of natural gas were $2/ MMBtu then the cost per tonne extracted would fall to $24. Again, this does not include the cost or penalty associated with compression. It may be possible to design the fluidized bed such that it runs at 10 bar pressure. This would reduce the compression penalty but change the energy balance of the process. As a comparison, if we were to calcine the limestone using nuclear electricity at 6¢/kWh we obtain an energy cost of $68 per tonne with no extra CO_2 produced. If the cost of electricity drops to 2.5¢/kWh then we obtain $27 per tonne extracted.

The Road Ahead

The feasibility of the system presented here can only be ascertained if more of the details are provided. Important questions are the energy requirements, the sorbent loss and environmental impacts. The first task is to begin a detailed investigation into the mechanics of an air contact system using sodium hydroxide solution as a sorbent. Based on initial analyses, we expect the cost of the air contacting to be small compared to the sorbent recycle system which discussed here[21]. This will require experimentation and theoretical analysis which is currently underway. The goal is to ensure the adequate supply of adsorbed carbon dioxide while keeping the infrastructure as small as possible. Given that the density of carbon dioxide is approximately $0.015 mol/m^3$, we would need an exposed area of ~20 m^2 with a wind speed of 6m/s and an efficiency of 50%. The system will also have to account for the intermittency of the wind.

There will also be process work and it is planned to use commercially available software, such as ASPEN™, to help in the analysis. This analysis will require some information regarding the extraction process, most obviously mass flow and pumping height. The only set quantities are the initial concentration, 370 ppm, and the pressure, which is atmospheric. One of the advantages of the air extraction option is that it can be sited to take advantage of site specific conditions. These may include temperature, wind, renewable energy potential, proximity to natural gas, proximity to sequestration site, and proximity to enhanced oil recovery site. In addition, the system should be design for ease of relocation. A logical option may be to site the extractor at the oil field in order to minimize transport. In such a case the oil could be reformed and used in the calcination system. These are all secondary considerations. The initial phase will involve starting with the basic principles of a rigorous absorber design. This will require adequate data for the kinetic reaction rate coefficients, the mass transfer coefficients, effective interfacial area, physical solubility, and the effective diffusivities of the various reactants[22].

Despite the low concentration of carbon dioxide in air and system constraints, there is no fundamental reason why carbon capture from air is not possible. The system presented here will generate extra carbon dioxide but has been designed such that this carbon dioxide is not released to the environment. For the design presented here, the cost depends greatly on the availability of solid dense membranes through which oxygen ions can diffuse. It is also affected by the design of the fluidized bed. It is encouraging that the process is a net heat producer. It is of note that this design only sequesters 1,100 tonnes of carbon dioxide a year. As with energy consumption itself, a wide range of sequestration options will produce the most efficient resolution of the dilemma.

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